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Synthesis and characterization of the first adamantane-based poly(*p*-phenylenevinylene) derivative: an intelligent plastic for smart electronic displays

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Abstract

A novel poly(*p*-phenylenevinylene) (PPV) derivative containing adamantane substituent—poly(2-methoxy-5-adamantaneethyloxy-*p*-phenylenevinylene) (MAE-PPV) is synthesized through the Gilch route. Adamantane was incorporated into this polymer because of its rigid and spherical structure, which results in reduction of interchain interaction. MAE-PPV is solution processable and shows high photoluminescence intensity. This polymer also demonstrates good electroluminescene properties.

Keywords: Adamantane; Poly(*p*-phenylenevinylene); Photoluminescence properties; Electroluminescene device

1. Introduction

Monochrome emissive dot matrix displays based on polymer light emitting devices (LED) can be fabricated that are suitable for use in various smart electronic and display devices. Electroluminescene (EL) devices using conjugated polymers layers as emitting medium have become a subject of great interest, since the first report of EL in poly(*p*-phenylenevinylene) (PPV) in 1990 [1], due to their potential for use in large area flat display. These 'intelligent displays' can be manufactured by the incorporation of a packaged polymeric display into a module with drive electronics for substantially less than today's cost for the new millennium products. Luminescence quantum efficiency is a critical issue in successful design of smart electronic system. Although conjugated polymers suffer from considerably lower photoluminescence (PL) quantum efficiency, they remain interesting as EL materials because they promise to have superior processing and thermal properties.

One of the main barriers to high luminescence quantum yield in the conjugated polymers is aggregation quenching of the excited state [2] because the chromophores are not diluted as in the dye doped discrete molecular systems. The physical origin of aggregation quenching has been proven to be interchain interactions [3]. Polymer chain interactions can be prevented by increasing the space between the conjugated strands with bulky side chain substituents or by increasing the gap between conjugated chromophores within each polymer chain.

Poly(2-methoxy-5-cyclohexylmethyloxy-*p*-phenylenevinylene) (MCHM-PPV) has exhibited enhanced PL intensity compared with poly(2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylene) (MEH) [4]. It has been presumed that the enhancement in PL intensity is due to the reduction of main chain aggregation in MCHM-PPV. To study this aggregation effect further incorporating of a bulky globular adamantly group to PPV main chain was considered and its effect on the degree of main chain aggregation as well as on the PL efficiency of polymers were investigated.

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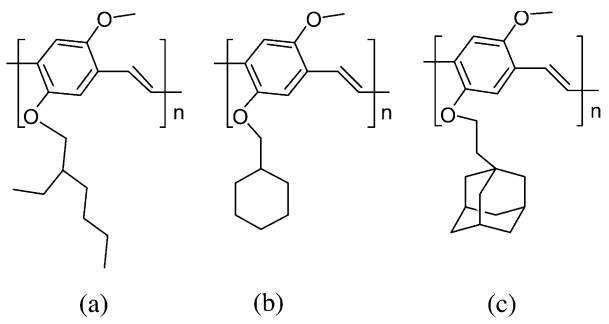

Fig. 1. Chemical structure of (a) MEH-PPV, (b) MCHM-PPV, and (c) MAE-PPV.

Therefore we report on the characterization of a new PPV derivative—poly(2-methoxy-5-adamantaneethyloxy-*p*-phenylenevinylene) (MAE-PPV) containing adamantane as a bulky substituent on the phenylene ring (Fig. 1). The incorporation of the adamantane substituent is expected to reduce interchain interaction.

2. Experimentals

2.1. Materials and instruments

4-Methoxylphenol, hydroquinone, sodium methoxide, 1-adamantaneethanol, potassium *tert*-butoxide, formaldehyde and 1,4-dioxane were purchased from Aldrich. Hydrochloric acid was bought from Duk-san Co. Ltd. Solvents and chemicals were used after proper purification according to conventional methods when required.

The substrate used in this study comprised of a glass coated with indium tin oxide (ITO). They were bought from Samsung corning Co. with the sheet resistance of 10 Ω/□. Polymer films were fabricated by the spin coating of MCHM-PPV and MAE-PPV on the substrate. In this process 0.5 wt.% (MAE-PPV) and 0.5 wt.% (MCHM-PPV) concentrations were used in chloroform solutions. Metal contacts were deposited on top of the polymer films via vacuum evaporation. Chemical shifts were reported in ppm units with tetramethylsilane as an internal standard when chloroform ($CDCl_3$) was employed as the solvent.

An O_2 plasma treatment for ITO was carried out by employing Precision 5000 plasma enhanced plasma chemical vapor deposition system provided by Applied Materials Corporation. The UV–Vis absorbance spectra were recorded using UV-3101PV, Shimadzu Co. The PL spectra were measured by using the PL-system equipped with a Spex 500M monochrometer, photomultiplier and Coherent Innova 90 Ar+ ion laser (488 nm).

The current–voltage (*I–V*) characteristics of device were measured using the Keithley 230 programmable voltage source and Keithley 195 A multimeter.

2.2. Synthesis

Fig. 2 outlines the preparation of MAE-PPV. Treatment of 4-methoxyphenol with 1-adamantaneethyl-*p*-toluenesulfonate (1) resulted in the formation of 1-methoxy-4-(1-adamantaneethyloxy)benzene (2). Bischloromethylation was performed on using 37% aqueous formaldehyde solution and 35% hydrochloric acid solution to afford 2,5-bis(chloromethyl)-1-methoxy-4-(1-adamantanethyloxy)benzene (3). Polymerization of the monomer (3) was accomplished by treating with potassium *t*-butoxide to obtain the polymer (4).

3. Results and discussion

3.1. PL intensity experiment

Using the facilities and procedures explained in the experimental section the PL spectra and absorbance of

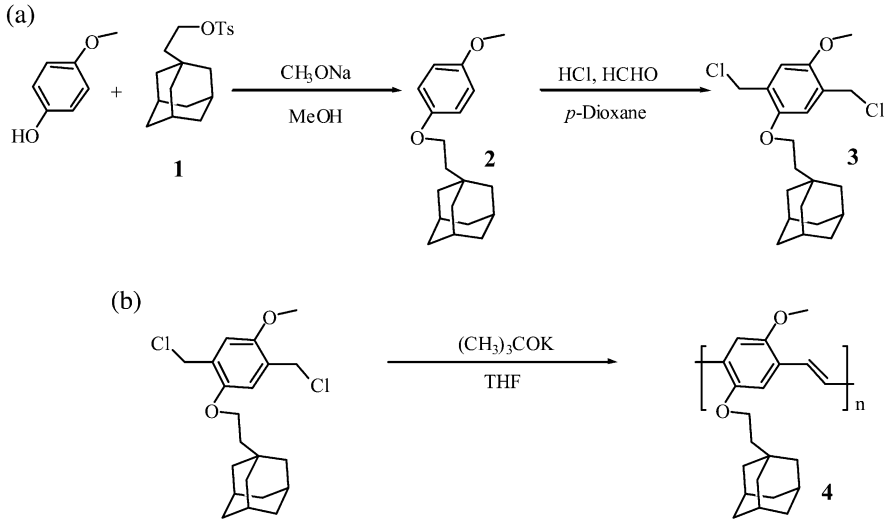

Fig. 2. Synthetic route of (a) monomer 3 and (b) polymer 4.

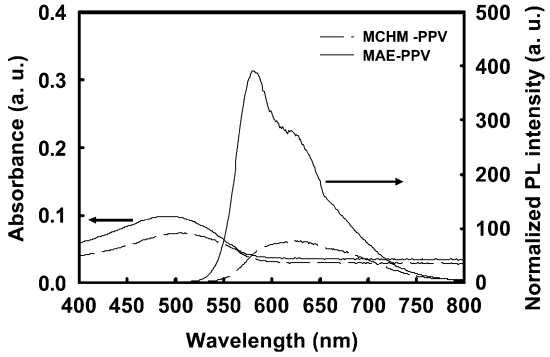

Fig. 3. The absorbance and PL spectra of MAE-PPV and MCHM-PPV.

the polymer were measured. As shown in Fig. 3, PL spectrum peaks of MCHM-PPV and MAE-PPV appear at 625 and 578 nm, respectively. MAE-PPV peak is approximately 50 nm blue shifted compared with its counterpart MCHM-PPV.

This is perhaps due to the steric effect of the adamantine group that reduces the effective conjugation length. Moreover, we observed much greater PL intensity (more than four times) for MAE-PPV compared with MCHM-PPV which has already shown greater PL intensity against MEH-PPV. The high PL intensity for MAE-PPV may also be due to the steric effect of the adamantane group, which can prevent interchain interaction, induced by closely packed emissive segments. It has been reported that closely packed conjugation polymers are prone to the formation of exciplexes or polaron pairs that can serve as quenching sites [5,6].

3.2. Current–voltage (I–V) characteristics and light emitting experiments

The typical current–voltage (I–V) characteristics of the single layer LED of an ITO/MAE-PPV/Al is shown in Fig. 4. The thickness of MAE-PPV was 110 nm. The

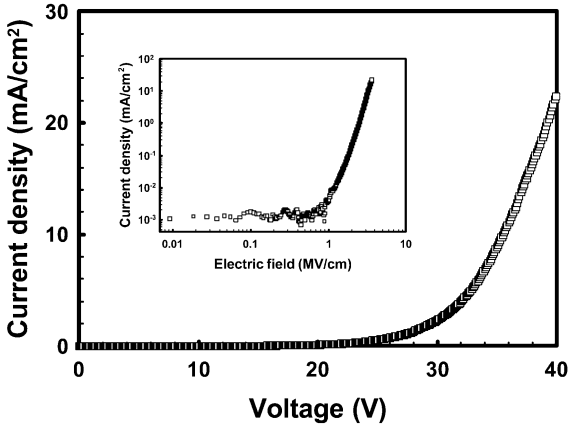

Fig. 4. I–V characteristic of an ITO/MAE-PPV/Al device. The inset shows the current density–electric field relation in log–log plot.

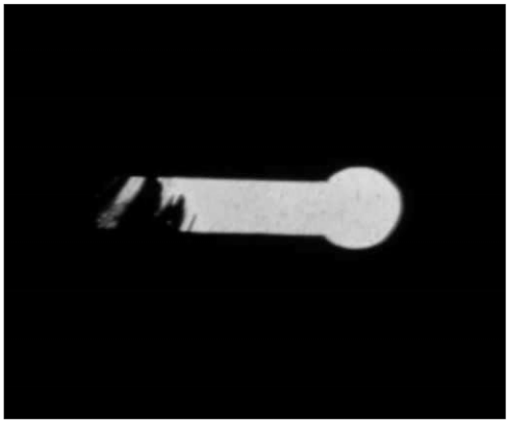

Fig. 5. Photograph of an ITO/MAE-PPV/Al device at 15 V.

inset shows the current density vs. electric field relationship of a device with a single layer. As can be seen in the inset of the figure, effective injection of holes of this device appears at 1 MV/cm. A photograph of an ITO/MAE-PPV/Al single layer device is shown in Fig. 5.

Fig. 6 is a log I–log V representation of Fig. 4. At low voltage (0.1–10 V), I–V indicates ohmic behavior, while at high voltage (10–40 V) the current follows the I–V^m relation with $m=7$. This indicates that the current is primarily limited by traps and space–charge limited current effects in the MAE-PPV layer as shown in Fig. 6 in which the power law dependence indicates of trapped charge with limited current observed for at least four orders of magnitude current in the current region.

4. Conclusion

We have reported the synthesis of MAE-PPV as the first material of adamantane-based PPV derivatives. Due to the steric effect of adamantane, the polymer shows very high PL intensity and blue shifts. This new material also demonstrated good EL properties.

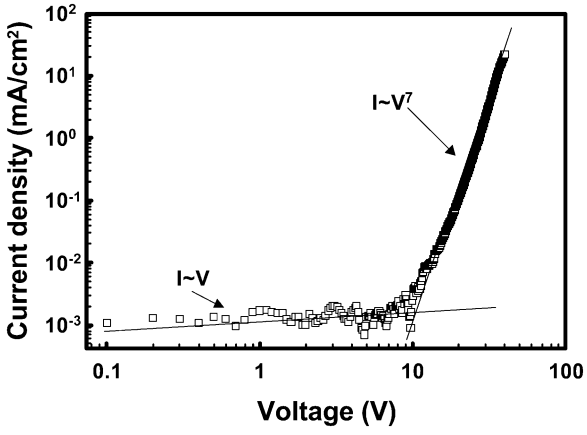

Fig. 6. Log I–log V characteristic of an ITO/MAE-PPV/Al device.

Acknowledgments

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References

[1] R.H. Friend, R.W. Gymer, A.B. Holmes, Nature 397 (1999) 121.

[2] M. Yan, L.J. Rothberg, F. Papadimitrakopoulos, M.E. Galvin, T.M. Miller, Phys. Rev. Lett. 73 (1994) 744.

[3] M. Yan, L.J. Rothberg, E.W. Kwock, T.M. Miller, Phys. Rev. Lett. 75 (1995) 1992.

[4] D.J. Choo, A. Talaie, Y.K. Lee, J. Jang, S.H. Park, G. Huh, K.H. Yoo, J.Y. Lee, Thin Solid Films 363 (2000) 37.

[5] S.A. Jenekhe, J.A. Osaheni, Science 265 (1994) 765.

[6] L.J. Rothberg, M Yan, F. Papadimitrakopoulos, M.E. Galvin, E.W. Kwock, T.M. Miller, Synthetic Metals 80 (1996) 41.